“Synthesis and Characterization of Polymer Grafted Carbon Nano Particles”

Summary of Work (5000 Words)

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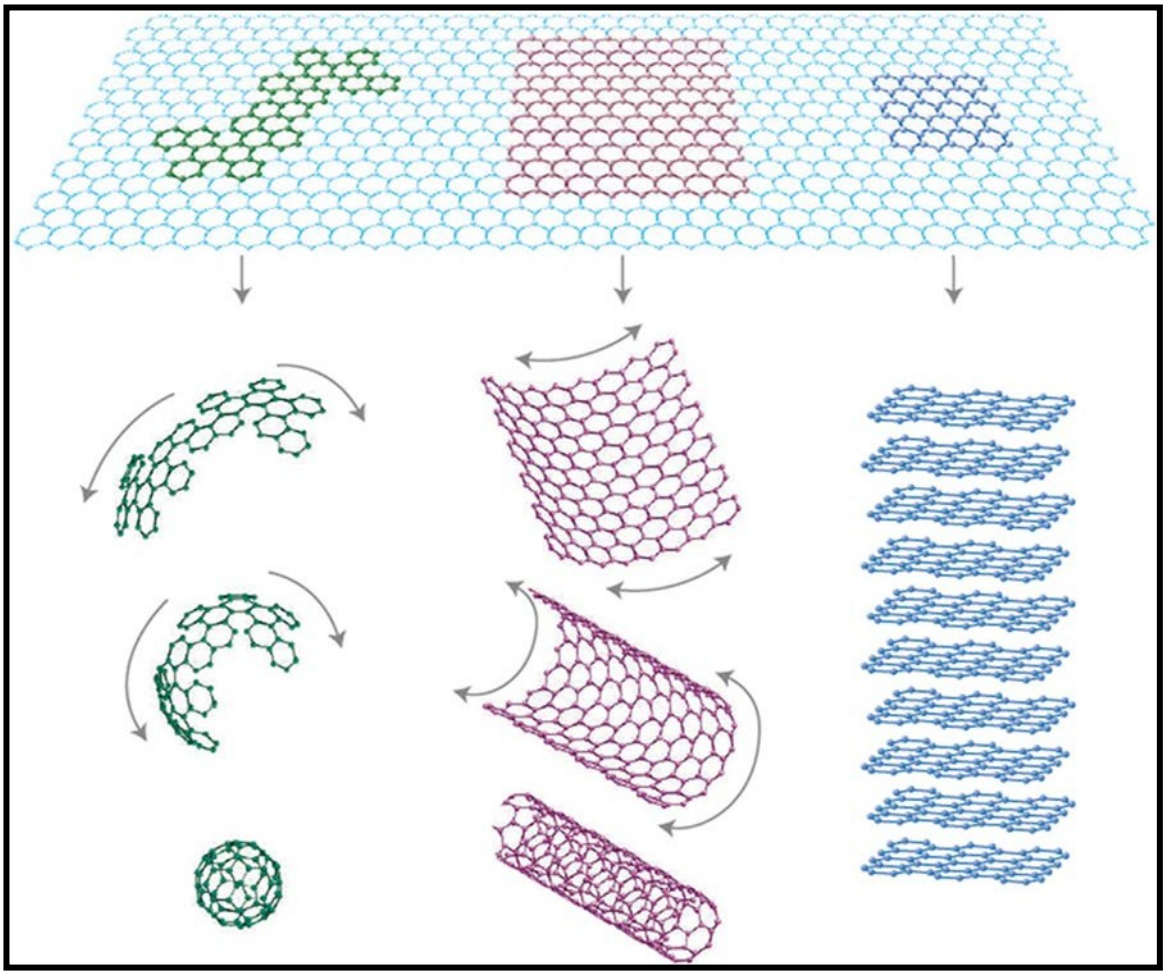
CONTENTS	Page No
Chapter 1-Introduction	3 - 8
Chapter 2	9 - 18
Chapter3	19 - 24
Chapter 4	25 - 28
Chapter 5	29 - 30
List of Publications	31

CHAPTER 1- Introduction:

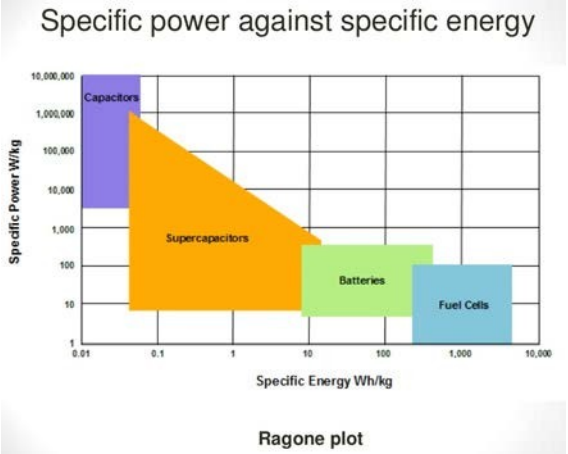
The unique features of carbon based nano materials originate from their high specific surface area, electrical conductivity mechanical properties and in some cases easy and cost effective preparation from readily available raw materials.[1,2,3] Carbon materials of different architectures and dimensionalities such as spherical (0D), for example fullerenes or Carbon nanodots; rod or fibre like (1D), for example carbon nano tubes (CNT); sheet like (2D), for



Scheme-1.1 Graphene is a 2D building block for carbon materials of all other dimensionalities. It can be wrapped up into 0Dbuckyballs, rolled into 1D nano tubes or stacked into 3D graphite

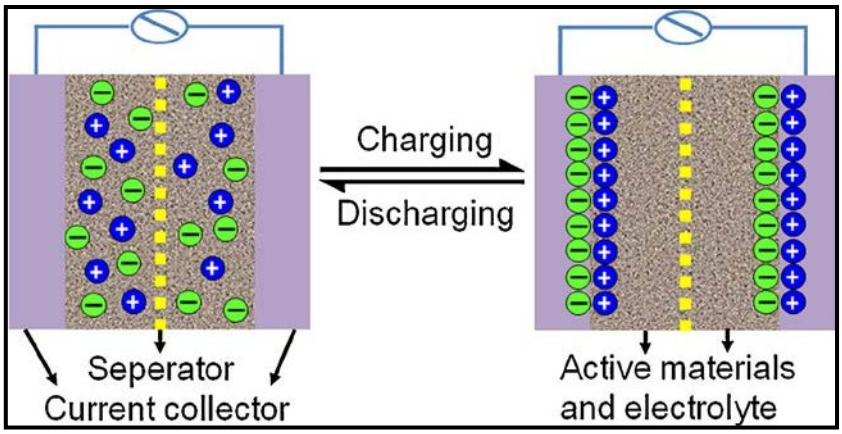
used widely for different applications ranging from catalysis, chemical separation, drug delivery to optoeletronic and energy storage applications.[1,4] Fullerenes are widely used in lubrication, super conductivity or drug delivery because of its shape and electronic arrangements which favour superconductivity under low temperature or chemical reactivity allowing attachment of different chemical moieties[5,6]. On the other hand very high conductivity, high aspect ratio, mechanical strength make CNT most effective light material

with great toughness.[4] However, expensive method of preparation is the major bottleneck during application of these materials.



Scheme1.2 Simplified Ragone plot of the energy storage domains for the various electrochemical energy conversion systems compared to an internal combustion engine and turbines and conventional capacitors.

In this respect two dimensional GNS have drawn considerable attention since the work of Geim and Novoselov in 2004[7] due to very much cost effective method of preparation from readily available raw materials. GNS are two dimensional stacks of sp^2 hybridized carbon atoms having single atom thickness. This results in very high surface area to volume ratio of GNS along with extremely high electrical conductivity and mechanical strength. These properties collectively make GNS as acceptable alternative of very much expensive CNT for many applications. High specific surface area (SSA) of GNS is very much desirable in catalysis or energy storage applications. However the stacking (leading to lowering in effective SSA) between the single graphene sheets and significantly high hydrophobicity often through challenges for different applications.[8] The energy storage in carbon materials operate through electrochemical double layer formation on the active material surface. Therefore, higher SSA is desirable for having greater value of specific capacitance. A schematic representation of capacitor action operating through electrochemical double layer capacitance (*EDLC*) is shown in Scheme 1.2 and equations of relevant parameters are given in eq. 1.1,1.2,1.3. Supercapaciter is an excellent energy storage device which bridge between capacitors and batteries. Theoretical capacitance of graphene is appreciably high about 550 F/g,[9]

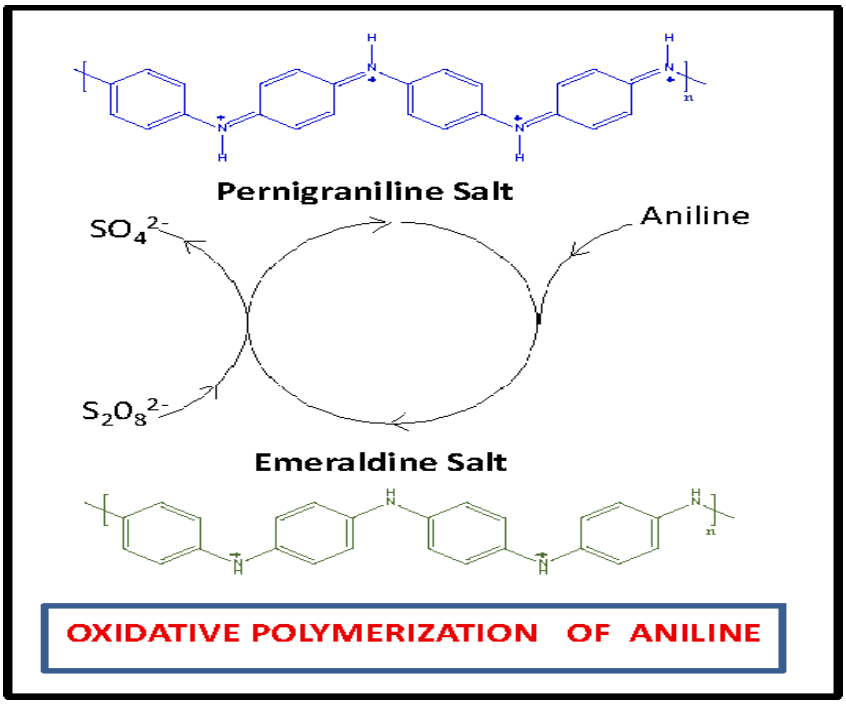


Scheme-1.3 Schematic illustration of the charging/discharging process in a supercapacitor.

however this cannot be achieved in practice due to poor exposed surface area in effect of (π-π) stacking of thesheets.

Conducting polymers or metal oxides having different available oxidation states are also capable of charge storage due to redox electron at the electrolyte-electrode surface.[9] This phenomenon is known as pseudocapacitance. Polyaniline (PANI) has attracted considerable attention in this respect due to its simple and cost effective method of preparation and availability of its different oxidation states.[10] The specific capacitance offered by PANI is appreciably higher than carbon based materials but slower rate of electron transfer and poor mechanical stability of PANI leads to poor rate capability and cycle life in case of purely PANI based electrodes. Therefore, integration of carbon based materials and PANI keeping their best synergy should produce hybrid electrode materials offering high energy density, power density and cycle life.

Nano structuring of electrode materials is desirable due to higher SSA and lower diffusion path length, allowing more efficient use of electrode surface and faster energy delivery.[11] Zero dimensional graphene oxide quantum dot (GQD) supramolecularly attached with PANI nano rods[12] have reportedly produced very high specific capacitance. Similarly, carbonized GQD used as electrode performed efficiently.[13] Literature reports significant improvement in performance of nano structured PANI as electrodes compared to randomly connected PANI chains.[14] Therefore, in the present thesis effort has been made for the construction of nano structured PANI on carbon nano materials with covalent connection to have best synergy and stability of the components. The reported mechanistic investigations of oxidative polymerization of aniline shows existence of induction period, during which oligomeric units are generated and then rapid growth of PANI chains on these oligomeric units occur following an autocatalytic mechanism (Scheme 1.4).



Scheme1.4 Mechanism of Oxidative Polymerization of Aniline

Therefore, in our view, keeping previously synthesized aniline oligomers present during onset of polymerization, chain growth may be induced to occur only from them. Thus, a control over the number of chains and length (function of [aniline]/[oxidant] ratio) may be affected. Following this strategy a general protocol for the controlled synthesis of PANI has been developed. Aniline oligomers are coupled covalently on carbon materials of different dimensions, subsequently oxidative polymerization is carried out to generate carbon/PANI nano structured hybrid materials.

Specific capacitance $C_{sp}(F\ g^{-1})=4C/m$ .....(1.1)

Energy density $E=(CV^2)/2$ .....(1.2)

Power density $P=V^2/(4R_S)$ .....(1.3)

The present thesis is composed of five chapters. **Chapter 1** presents the introduction and forewords in the field of carbon/PANI nanostructured materials. **Chapter 2** presents controlled polymerization of aniline following a *'grafting from'* strategy initiated from aniline trimer (APQD) anchored carbon nanodot surface which are isolated after oxidation of readily available candle soot followed by size separation. This chapter demonstrateswell

controlled spherical CND-g-PANI nano particles having sizes in the range of (10-15) nm which are synthesised from precursor spherical carbon nano particles having average size of ~ 2.3 nm. The nano structured CND-g-PANI show very high specific capacitance of ~ 972 F/g with about 93% stability after 2000 charge discharge cycles compared to ~399 F/g with about 65% cyclic stability in case of prepared non covalently attached CND/PANI nanocomposite.

Chapter 3 discusses the controlled grafting of PANI chains from GO nanosheet surface following 'grafting from' approach initiated by APQD attached GO nano sheets. The resulting GO-g-PANI nano composites show interesting morphology and improved charge storage property compared to the non covalently attached GO/PANI composite.

In **Chaper 4** synthesis of covalently attached enantioselective PANI chains on the graphene oxide nano sheets has been carried out in presence of chiral dopants like D or L-camphorsulphonic acid. Covalent attachment of the helical PANI chains on the GO nano sheets has been ensured by initiating the polymerization from APQD moieties attached on GO sheets. The characterization of the induced chirality has been carried out by circular dichroism (CD) and FESEM techniques. Apart from ensuring covalent attachment, initiation from the APQD moieties attached on the GO sheet has shown remarkable effect on the chirality of the synthesized PANI chains. Improved energy storage property has been shown by the synthesized chiral nano composites, which is attributed to their unique morphology. The nano composite should also be very much effective in chiral separation. Details of synthesis, characterization and applications of the synthesized chiral nano composites are reported in thischapter.

Chapter 5 presents the summary of the work and possibilities for future extension of the concept developed for the development of novel functional materials.

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14. Y.-G. Wang, H.-Q. Li, and Y.-Y. Xia, *Adv. Mater.* **2006**, *18*, 2619–2623

CHAPTER – 2

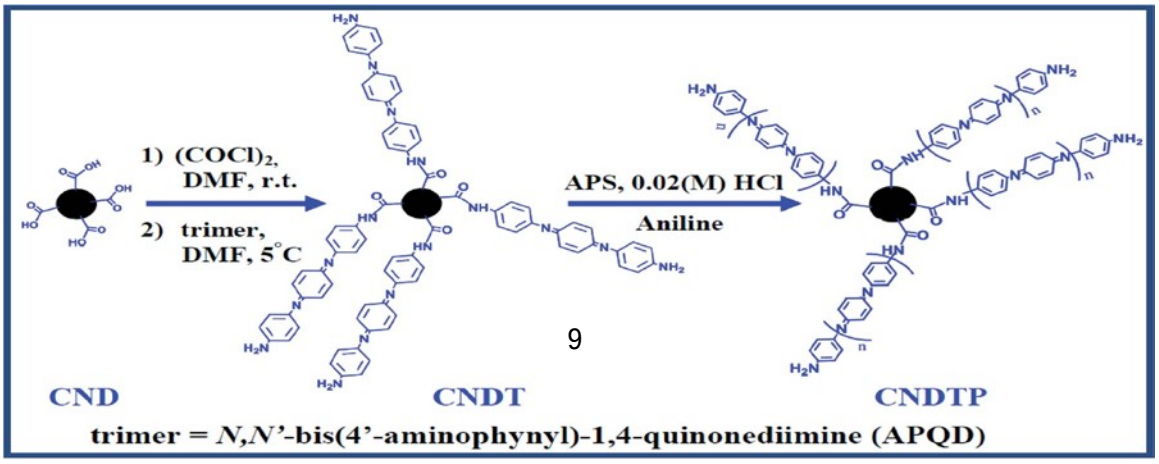
Candle soot derived carbon nanodot/polyaniline hybrid materials through controlled grafting of polyaniline chains for supercapacitors

Introduction:

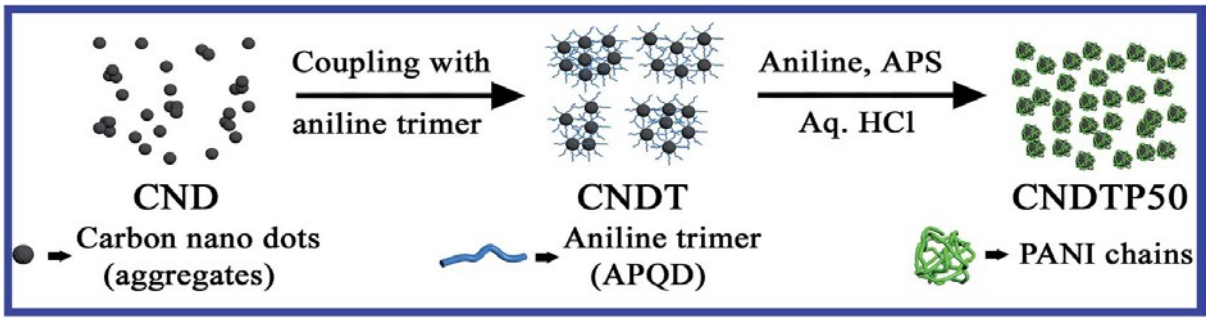
Spherical carbon nano dots (CNDs) having diameter less than 10 nm, may function as very nice nano templates for the isotropic growth of PANI chains. Lower degree of inter particular stacking of spherical CNDs compared to the sheet like graphene quantum dots (GQDs) is an added advantage. However, literature shows many reports for the synthesis of sheet like GQDs and formation of GQD/PANI nano composite for energy storage applications. In this respect, report of CNDs in composite formation with PANI is scarce. Inorder to retain the effect of nano structuring of CNDs, a grafting from strategy for the controlled growth of covalently attached PANI chains from CND surface is carried out in this work. The CNDs are prepared through oxidation of readily available candle soot, followed by size separation. After this oligomeric aniline moieties are coupled on CND surface and then oxidative polymerization of aniline is carried out. The growth of PANI chains occur preferentially from those sites due to their much lower oxidation potential compared to monomeric aniline. The nano structured core-shell like CND-g-PANI synthesized show very interesting morphology and remarkably improved specific capacitance which are thoroughly studied.

Results and Discussions:

The schematic representations of controlled growth of PANI from CNDs and their morphological developments are shown in Scheme 2.1 and 2.2.



Scheme2.1 Controlled grafting of PANI chains on the CND surface following a 'grafting from'approach.



Scheme 2.2 Schematic representation of the controlled growth of PANI chains on CNDs.

The excitation dependent emission of aqueous CND solution, very small sizes as apparent from histogram of HRTEM and AFM analysis (average size ~ 2 nm, height ~ 0.85 nm) in Figure 2.1, establish formation of spherical carbon quantum dots or carbon nano dots (CNDs).

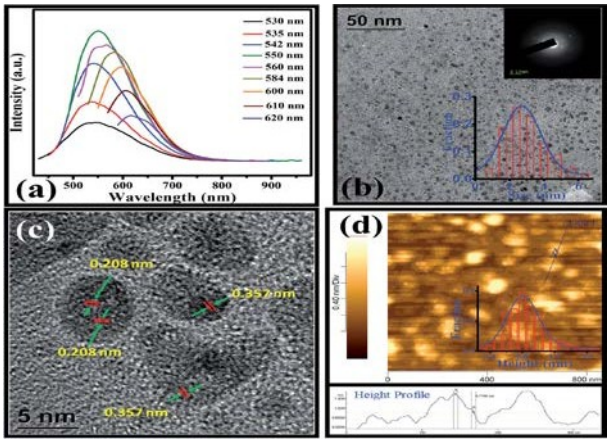


Figure 2.1 Characterization of synthesized CNDs (a) PL ,(b) TEM ,(c) Lattice Fringes in HRTEM, (d) AFM

The anilide group formation with APQD in CNDT is confirmed by the appearance of a signal at 1658 cm^{-1} with complete disappearance of carboxylic carbonyl group which is present at 1728 cm^{-1} in CND in the IR spectra[3] in Figure 2.2. The signals in the range of 1584-805 cm^{-1} confirms formation of PANI chains in CNDTP50(1) andCNDTP50(1)R.

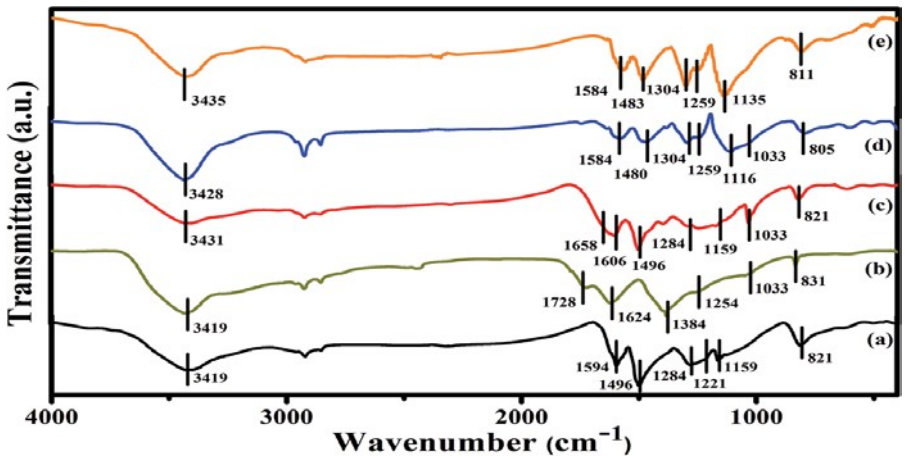


Fig. 2.2 FTIR spectra (a, b, c, d and e) for APQD, CND, CNDT, CNDTP50(1) and CNDTP50(1)R samples respectively.

The XPS analysis in Figure 2.3 confirms the attachment of APQD moieties in CNDT by the appearance of N(1s) signal. In case of CNDTP50(1) and CNDTP50(1)R, the proportion of N atom increases due to formation of PANI chains and in CNDTP50(1)R relative increase in (C/O) ratio compared to CNDTP50(1) confirmsdeoxygenation.

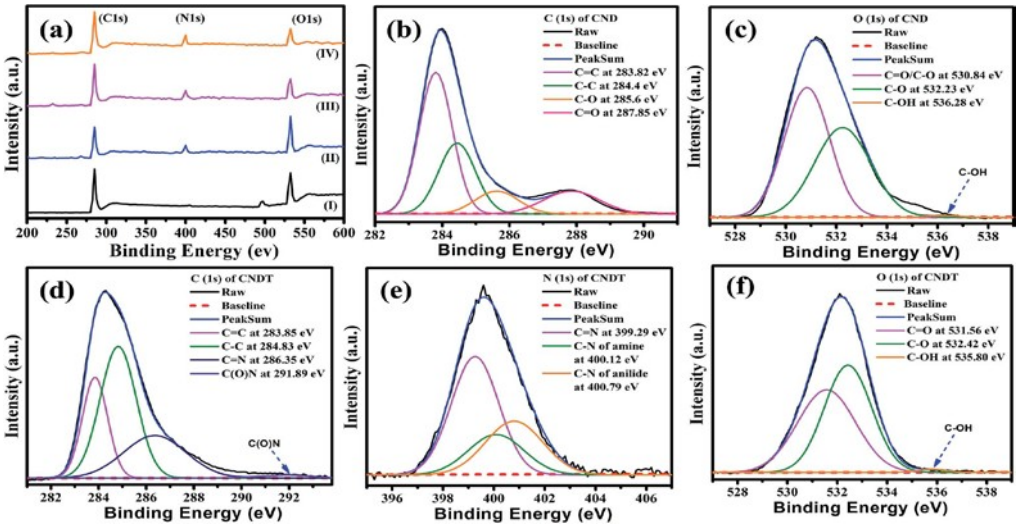


Figure 2.3 XPS analysis of (a) CNDs, CNDT, CNDTP50(1) and CNDTP50(1)R from (I) to (IV) respectively

Figure 2.4 shows the overlay of aniline polymerization kinetics determined from the absorbance at 650 nm at different time intervals during polymerizations. Representative UV spectra for CNDTP50(1) and CNDP15 are given in Figure 2.5. The overlay of polymerization kinetics in Figure 2.4 confirms there is no induction period during polymerizations in presence ofCNDT.

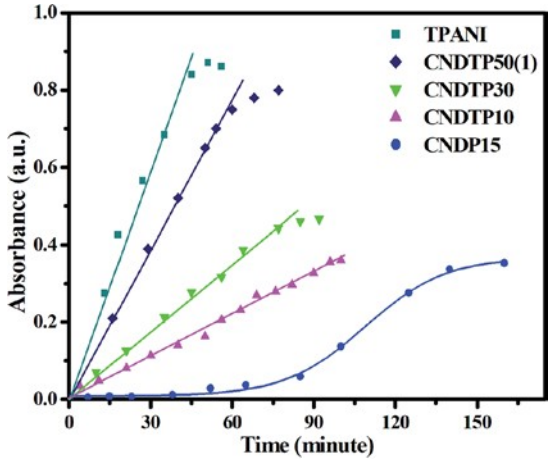


Figure 2.4 Kinetics of oxidative polymerization of aniline 10 mg APQD used for TPANI and for rest the number represents , 50 mg CNDT, 30 mg CNDT, 10 mg CNDT and 15 mg CNDs, for TPANI, CNDTP50(1), CNDTP30, CNDTP10 and CND15 respectively.

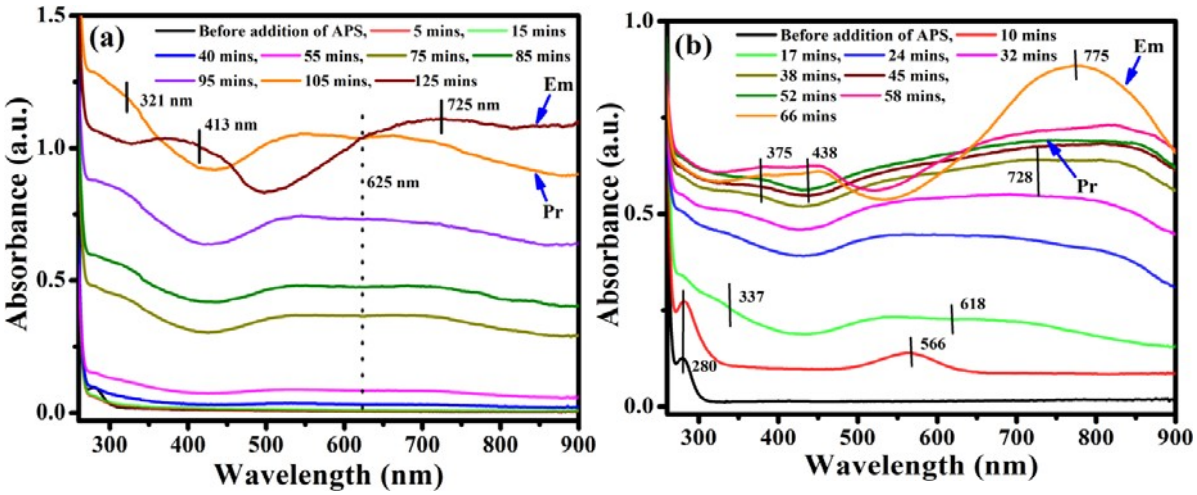


Figure 2.5 UV spectra during aniline polymerization for (a)CNDP15, (b) CNDTP50(1) system

The AFM analysis (Figure 2.6) of CNDTP50(1) sample at 40% and 75% conversion [CNDTP50(2)] of aniline shows gradual increase in height unlike uncontrolled PANI growth in CNDP15. This further confirms the controlled chain growth of PANI.

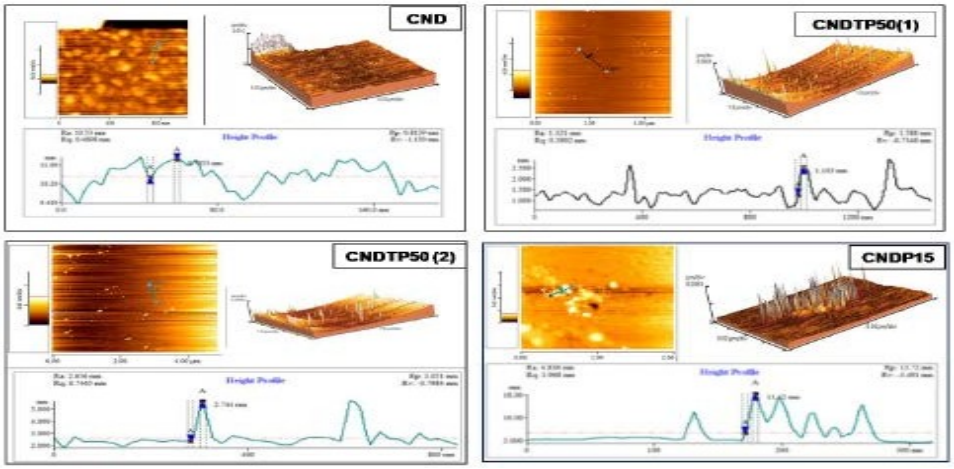


Figure 2.6 AFM analysis of CND, CNDTP50(1), CNDTP50(2), CNDP15

In Figure 2.7, candle soot shows signals at 1348 and 1590 cm^{-1} corresponding to D and G bands, I_D/I_Gratio is 0.76 where in CND ratio is 0.8. In APQD these signals are red shifted, ratio is 0.89. This ratio is 0.78 for CNDTP50(1)R compared to 0.91 of CNDTP50(1) indicating uniform sized π-stacked CND-g-PANIsurface.[6]

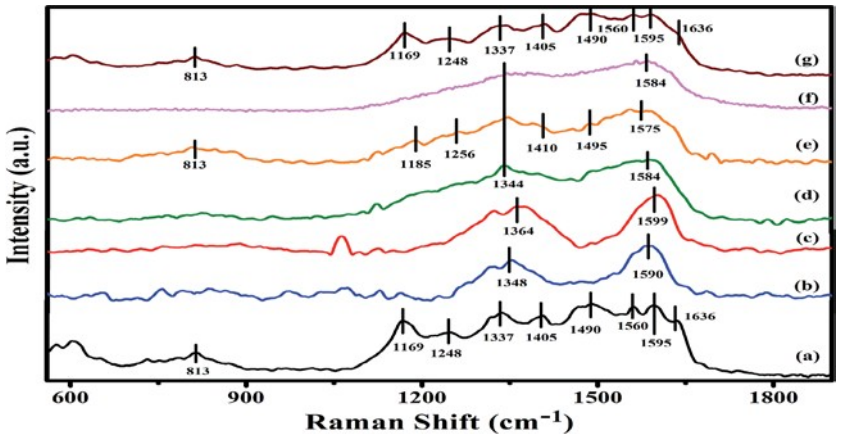


Fig. 2.7 Raman spectra of (a) PANI, (b) candle soot, (c) CNDs, (d) CNDT, (e) CNDTP50(1), (f) CNDTP50(1)R and (g)CNDP15.

In WAXS analysis (**Figure 2.8**), signals of CND indicates increased distancebetween (002) planes and (101) planes due to oxidation compared to candle soot. In CNDT the (002) plane shows a significant shift to 2θ = 22.64 with broadening of the peak indicating an appreciable amount of interaction between the CND surface and APQD moieties possibly through (π–π) stacking by their aromatic rings. Relatively sharp signals for PANI are observed at 2θ = 15.56, 20.55, and 25.83 corresponding to (011), (020) and (200) crystal planes.[7]In the case of CNDTP50(1), both of the signals at 20.57 and 25.72 are relatively sharp.InCNDTP50(1)Rthesignalsat44.24,24.64,21.58areattributedtothe(101)and (002) graphitic planes(020) plane of PANI respectively.

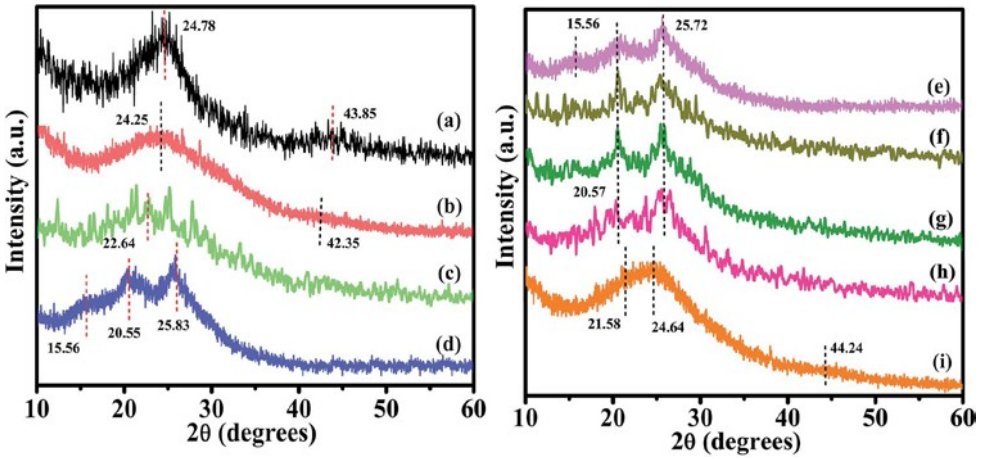


Fig. 2.8 Wide angle X-ray diffraction (WAXS) analysis of (a) candle soot, (b) CNDs, (c) CNDT, (d) PANI, (e) CNDTP10, (f) CNDTP30, (g) CNDTP50(1), (h) CNDP15, and (i) CNDTP50(1)R.

The FESEM in **Figure 2.9** shows very small 'coffee seed' like spherical CND particles. The particle size increases in CNDT and in cases of CNDTP10 and CNDTP30 relatively agglomerated morphology of PANI chains is observed. However, in CNDTP50(1) again discrete spherical morphology corresponding to CND quoted with PANI chains is observed. After reduction almost a similar morphology is maintained. The TEM analysis in **Figure 2.10** also shows a similar evolution of morphology as apparent from the FESEM analysis.

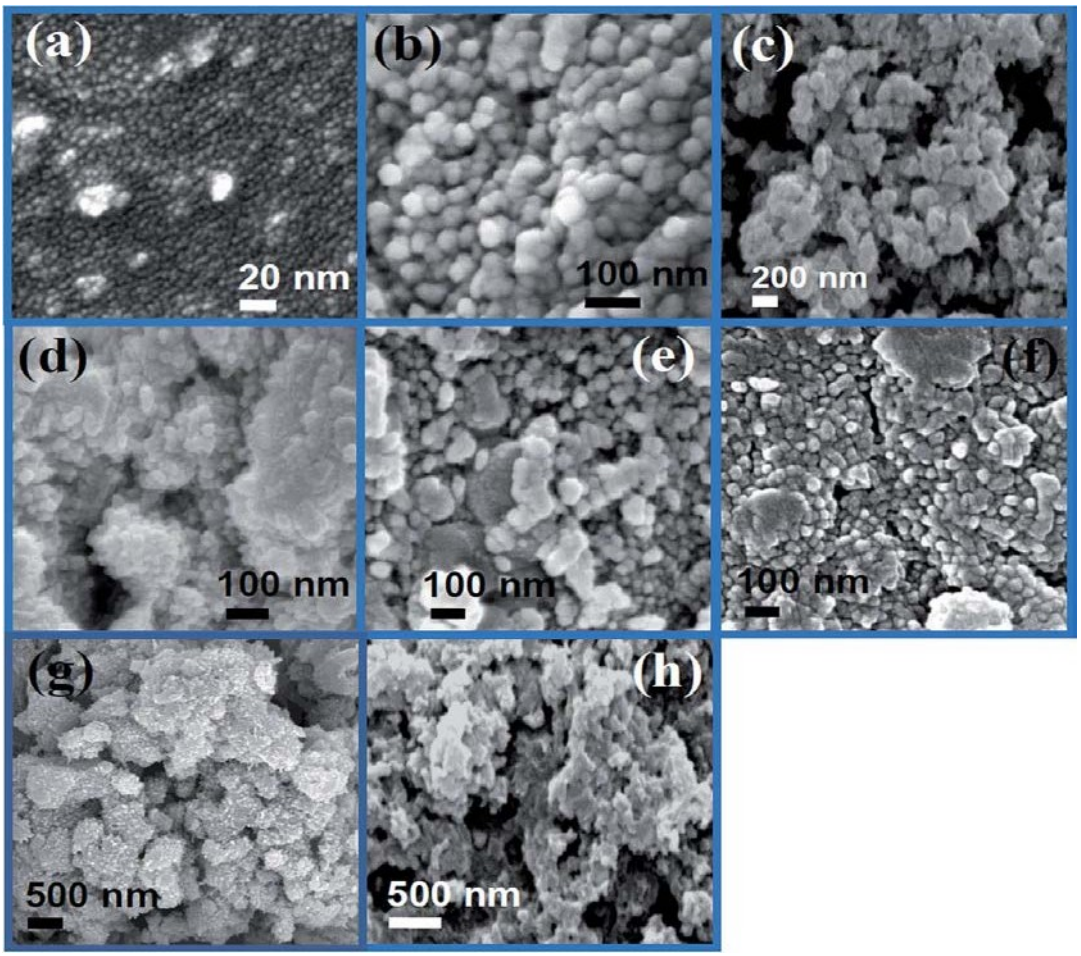


Fig 2.9 FESEM images of (a) CND, (b) CNDT, (c) CNDTP10, (d) CNDTP30, (e) CNDTP50(1), (f) CNDTP50(1)R, (g) CNTP50(2) and (h) CNDP15

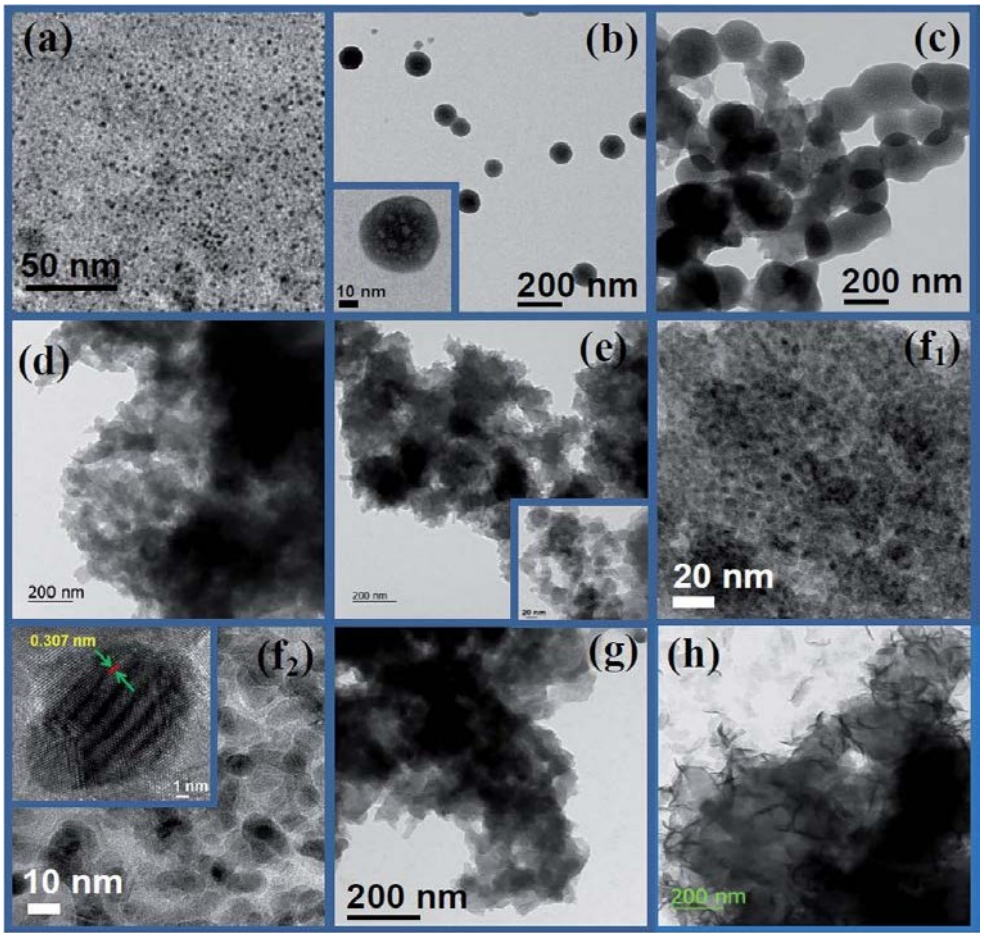


Fig. 2.10 TEM images of (a) CND, (b) CNDT, (c) CNDTP10, (d) CNDTP30, (e) CNDTP50(1), (f1 & f2) CNDTP50(1)R, (g) CNDTP50(2) and (h) CNDP15 samples cast from their dilute aqueousdispersion.

The analysis of specific surface area and porosity through N_2adsorption/desorption isotherm analysis is conducted as given in **Figure 2.11**, analysis of BET surface area and BJH pore volume, pore diameter is summarised and given in **Table 1.** The results are expected as many of the previous studies have reported a low SSA or porosity for the carbon nano-particles derived from candle soot. A further lowering in the SSA or pore volume is also reported upon surface modification through amide-amine type functionalization.[9] The adsorption isotherms for CNDP samples show a type-IV pattern indicating micro- and meso-porousmaterials.

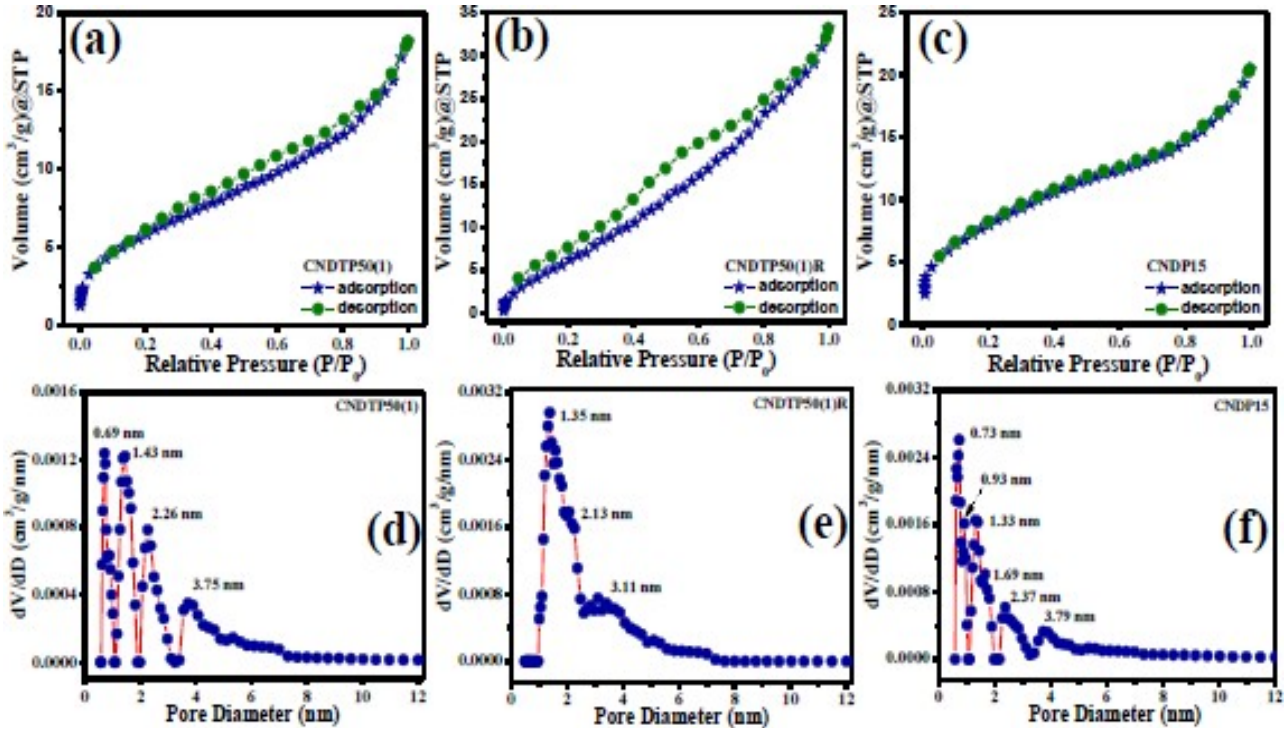


Figure 2.11: (a)-(c) represents N_2 adsorption/desorption isotherm and (d)-(f) pore size distribution (slit pore, NLDFT equilibrium model) of CNDTP50(1), CNDTP50(1)R, and CNDP15 respectively.

Sample	BET surface area (m^2/g)	Total pore volume (cc/g)	Pore diameter range (nm)
CND	13.38	0.051	(1.58-6.9)
CNDTP50(1)	22.58	0.028	(0.69-6.99)
CNDTP50(1)R	33.29	0.049	(1.35 - 6.68)
CNDP15	28.29	0.032	(0.73-4.46)

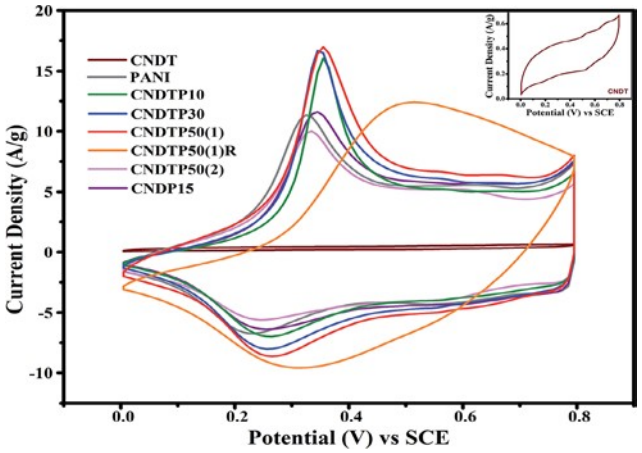


Fig. 2.12 CV curves recorded in 1 (M) H_2SO_4 at a scan rate of 10 mVs^{-1}. Inset shows the enlarged CV curve ofCNDT.

Significant increase in specific capacitance in cases of covalently grafted PANI systems (CNDTP systems) indicates better synergy between the components which reaches at maximum in CNDTP50(1)R sample due to much improved stacking between aromatic rings

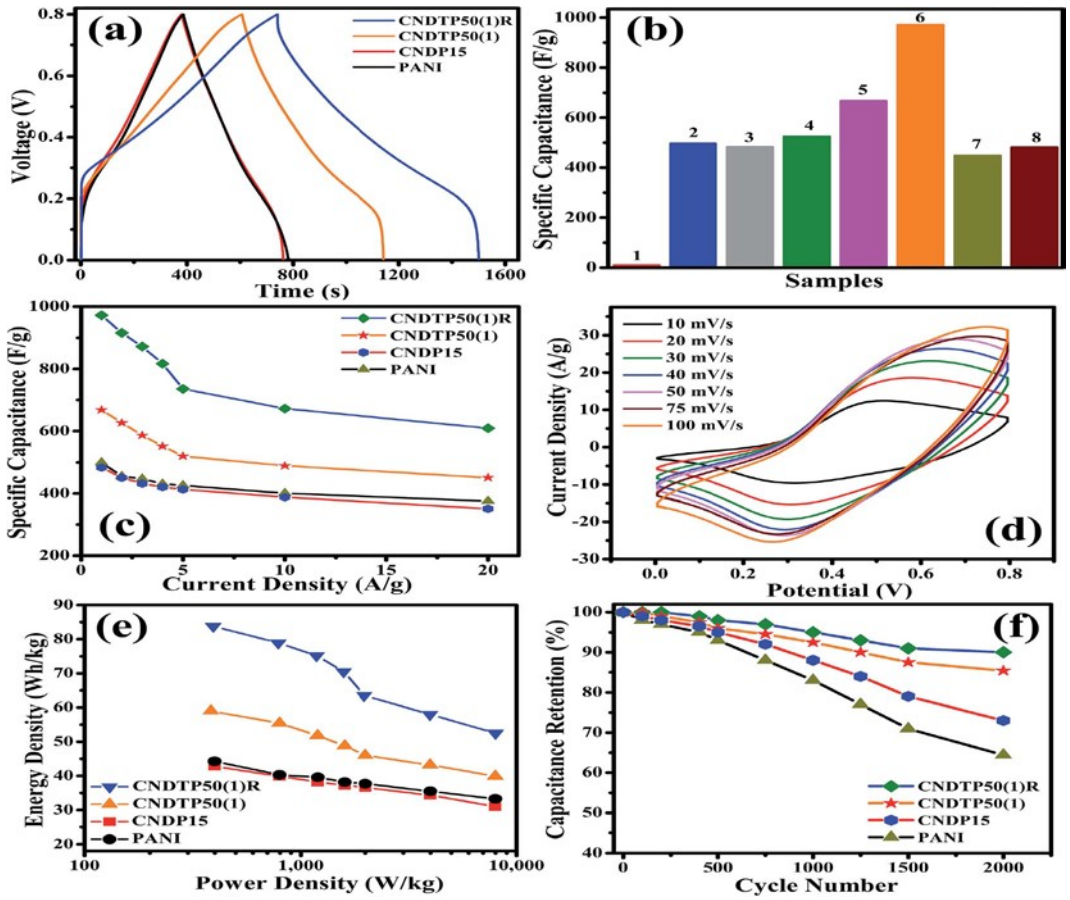


Fig.2.13 Electrochemical analysis of the samples. (a), (c), (e) and (f) represent galvanostatic charge/discharge curves, the plot of specific capacitance vs. current density, the Ragone plot andcyclic stability respectively corresponding to PANI, CNDP15, CNDTP50(1), and CNDTP50(1)Rsamples;(b)representsthesummaryofspecificcapacitanceforallofthe samples [(1) CNDT, (2) PANI, (3) CNDTP10, (4) CNDTP30, (5) CNDTP50(1), (6) CNDTP50(1)R, (7) CNDTP50(2), and (8) CNDP15] and (d) scan rate variation plots for the CNDTP50(1)R sample.

of PANI and CND surface. This is also evident from the GCD plots in **Figure 2.13**. Significant improvement in rate capability and cycling stability is attributed to the increase in conductivity of CND surface upon reduction and improved mechanical properties of PANI chains. This is also evident from the GCD plots in **Figure 2.13**. Significant improvement in rate capability and cycling stability is attributed to the increase in conductivity of CND surface upon reduction and improved mechanical properties of PANI chains.

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CHAPTER – 3

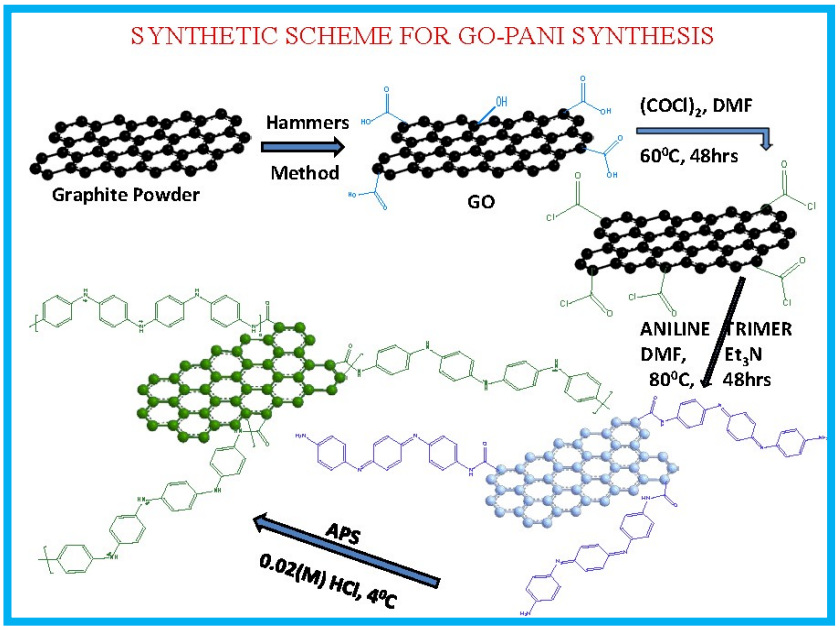
Controlled Synthesis of Nano Structured Polyaniline on Graphene Oxide Sheets for Efficient Energy Storage Application

Introduction:

The remarkable improvement in energy storage demonstrated in the previous chapter by CND-g-PANI nano particles originated primarily due to nano structured PANI formation; hence an effect primarily due to pseudocapacitance of PANI. Rate capability and cycling stability are two very important parameters for an efficient supercapacitor which develop from faster charge accumulation on the electrode surface during charging and mechanical stability alongside good conductivity of the electrode material.[1,2] These parameters are superior in carbon materials than PANI.[3,4] Hence in order to build a hybrid material electrode and to extract best synergy between the components it may be appropriate to grow PANI chains in controlled fashion on graphene nano sheet surface. The applicability of the developed protocol for controlled growth of PANI chains from an insoluble support in the previous chapter, is further tested here by the growth of 1D PANI nano cylinders from 2D graphene oxide (GO)sheets.

Results and Discussions:

The reaction scheme for controlled growth of PANI chains from GO surface are given in Scheme 3.1



Scheme 3.1 Synthetic Scheme for GOPANI

Figure 3.1(a) shows the polymerization kinetics of aniline in presence of different amount of GO sheets. The induction period is found to decrease gradually with increasing amount of GO, which is expected during oxidative polymerization of aniline in presence of heterogeneous surface.[5]

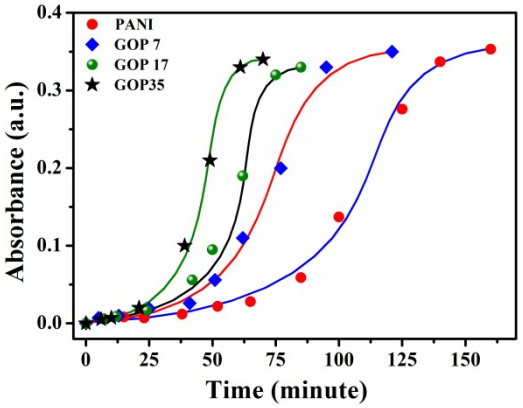


Fig 3.1(a) Polymerization Kinetics with GO

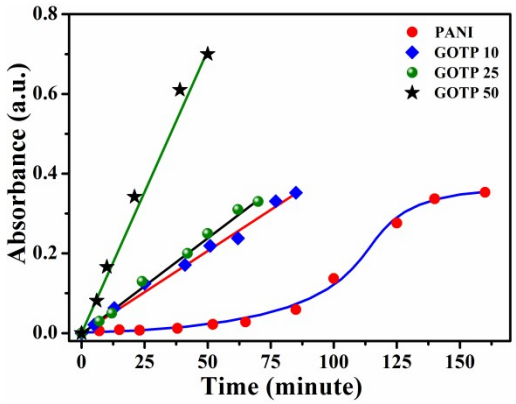


Fig 3.1(b) Polymerization Kinetics with GOT

This is in contrast with the plot in Figure 3.1(b) where no induction period is observed during polymerization in presence of APQD tethered GO (GOT). This indicates that chain growth occurs from the APQD moieties as soon as oxidant is added. In FTIR spectrum of various samples(as designated in the Figure 3.2). The disappearance of signal at 1722 cm^{-1} and development of a signal at ~1648 cm^{-1} in case of GOT than in case of GO, confirms the anilide group formation and hence attachment of APQD moieties on the GO surface.[6] The formation of PANI chains is confirmed in GOTP50 and GOTP50R from the signals in the range of 1579 cm^{-1} to 812 cm^{-1}. [7] The depression in intensity of the signal at 1269 cm^{-1} indicates decrease in population of epoxy groups in GOT50R sample which is produced after reduction of GOTP50 sample with aqueous hydrazine hydrate solution.

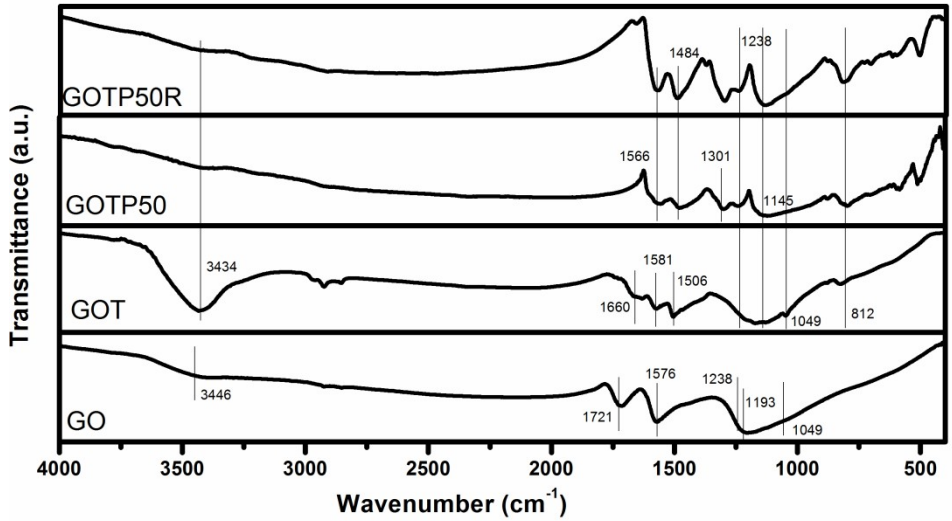


Figure 3.2 IR spectra of GO,GOT, GOTP50, GOTP50R

In wide angle X-ray scattering (WAXS) (Figure 3.3) indicates increase in distance between (002) planes in GOT from GO and appearance of signals at angles 25.63, 20.14 and 15.63 confirms PANI formation.[8] The increase in broadness of signals of GOTP50R compared with GOTP50 also indicates better (π-π) stacking between aromatic phenyl rings of PANI and those present on graphene oxide nano sheet surface.

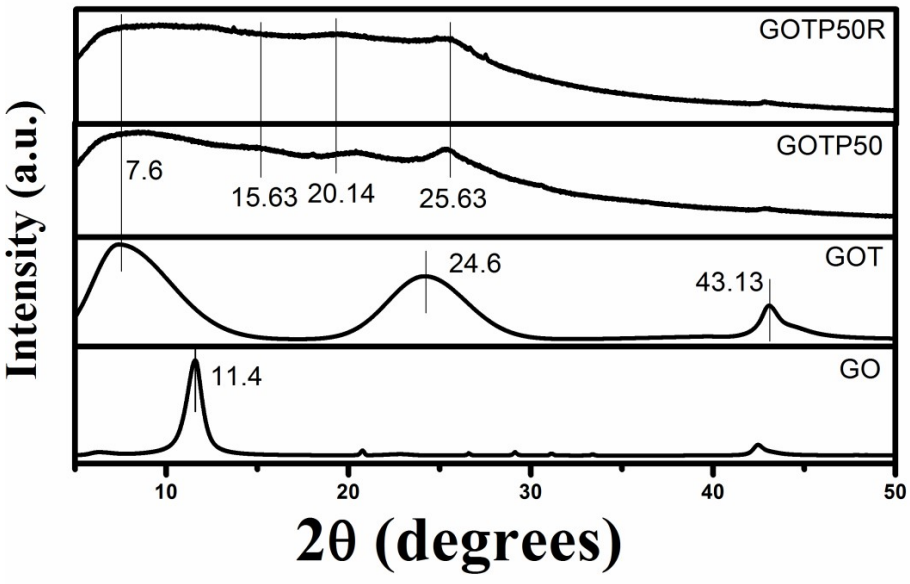


Figure 3.3 WAXS Spectra of GO, GOT, GOTP50, GOTP50R

The analysis of surface area through BET show relatively poor surface area of GOT which further decreases after PANI growth. Now, this is well reported in the literature that growth of PANI chains show decrease in surface area and porosity due to pore jamming of GO surface by PANI chains.[9] The relevant data is given in Table3.1.

Sample	BET Surface Area (m^2/g)
GOT	42.854
GOP35	25.645
GOTP50	15.452
GOTP50R	11.822

The morphological analysis through FESEM and HRTEM techniques are given in Figure 3.4 and Figure 3.5 respectively. The FESEM analysis shows in all the cases PANI nano cylinders are covering the GO nano sheets. However in cases of GOTP10 and GOTP25 formation of non grafted, randomly connected PANI fibres are observed. In GOTP50, GOTP50R and

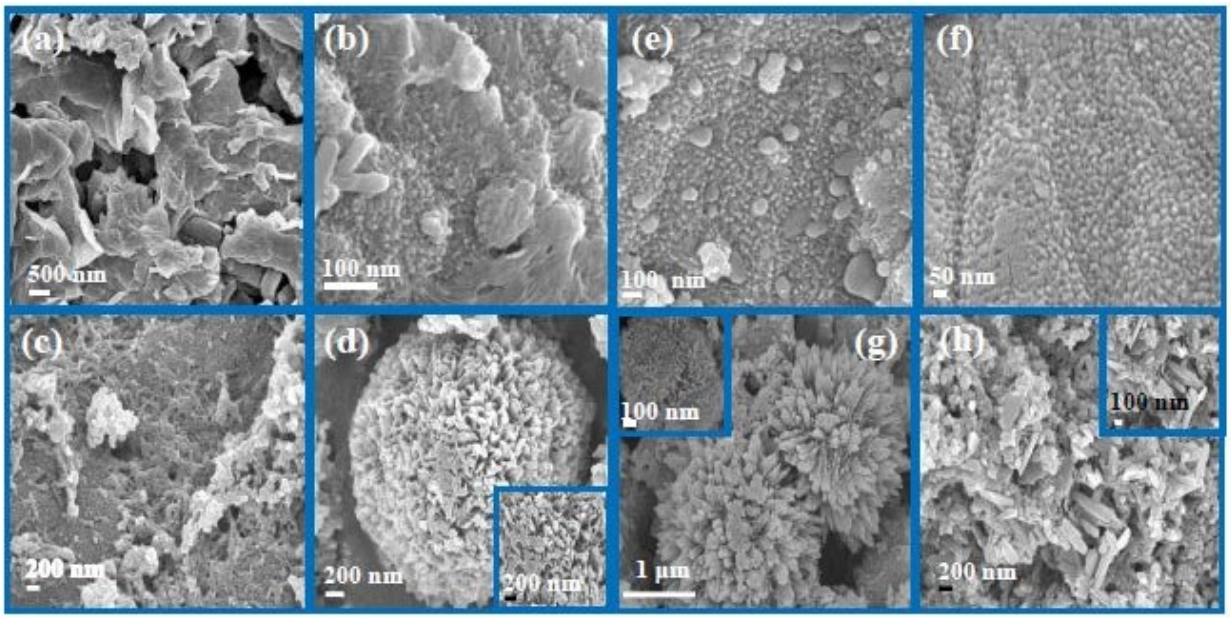


Fig. 3.4 FESEM images of (a) GOT, (b) GOTP10, (c) GOTP25, (d & e) GOTP50, (f) GOTP50R, (g) GOTP 100 and (h) GOP35

GOTP100 no such PANI chains are observed which is attributed to the much faster rate of polymerization in these cases compared to the earlier two cases, which excludes PANI formation through self nucleation. Apart from this, formation of '*marigold*' flower like structures or '*agave*' plant like structure is frequently observed in cases of GOTP50 or GOTP100 respectively. In case of GOP35 formation of randomly connected PANI fibres are observed along with a good number of GO nano sheets having surfaces without any PANI chain attachment. This clearly establish the fact that covalent attachment of PANI chains occur only when APQD moieties are attached with GO nano sheets. The HRTEM analysis supports the morphology observed in FESEM analysis with clearly visible PANI chain coated and non coated GO sheets of similar dimensions. The SAED pattern confirms the crystalline and amorphous nature of such domains as shown in the figure.

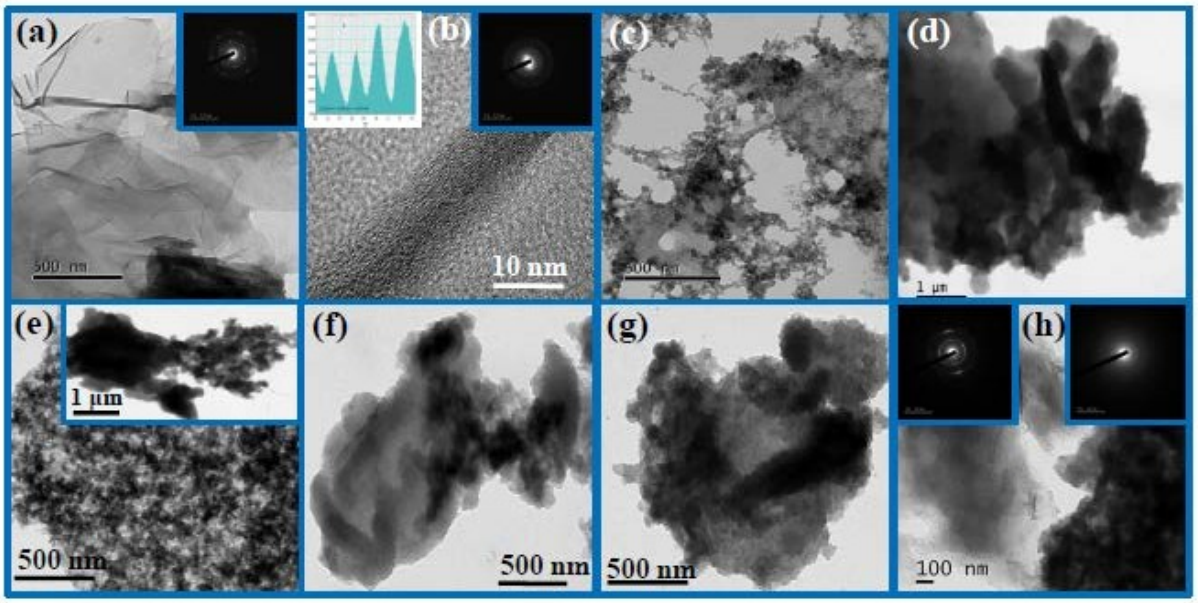


Fig. 3.5 TEM images of (a & b) GOT, (c) GOTP10, (d) GOTP25, (e) GOTP50, (f) GOTP50R, (g) GOTP 100 and (h) GOP35 samples cast from their dilute aqueous dispersion.

The cyclic voltametry analysis (in a 3 electrode configuration taking Ag/AgCl counter electrode and Pt wire as reference electrode in 1(M) H_2SO_4 as electrolyte) of these samples show the CV traces are rectangular in all of the cases indicating good charge flow across the electrodes. In addition, three peaks are observed, of which the peak at ~0.2V is attributed to the redox transition originated from the oxygenated functionalities present on the GO surface.

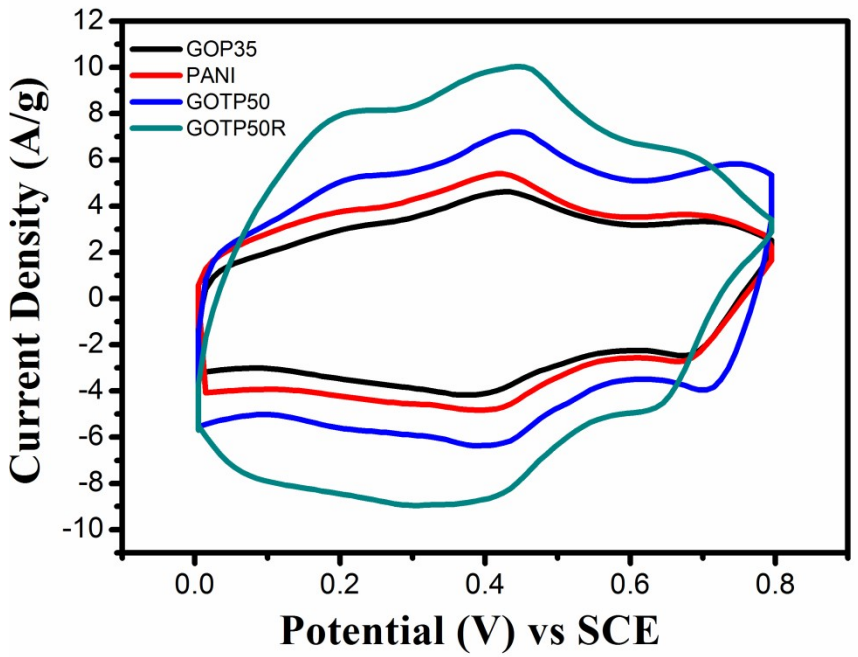


Fig 3.6 CV curves recorded in 1 (M) H_2SO_4 at a scan rate of 10 mVs^{-1}

The signal at ~0.4 V is due to leucomeraldine to emaraldine state transition of PANI and finally the signal at 0.6 V is attributed to the transition between emaraldine to pernigraniline form.[10] The area enclosed under the curve gradually increases from PANI and reaches the maximum in case of GOTP50R indicating increased specific capacitance. It is notable that despite containing equivalent amount of GO in samples GOP35 and GOTP50, the latter shows much higher specific capacitance than the former. This is attributed to the formation of covalently attached aligned PANI nano fibres. In case of GOTP100 in spite of formation of interesting nano structures, possibly the greater proportion of the poorly conducting GO nano sheets cause lowering of specific capacitance compared to GOTP50.[11] Maximum specific capacitance of 630 F/g is noted in case of GOTP50R with remarkable rate properties and cyclic stability which is attributed to the increased conductance and improved (π-π) stacking between PANI chains and GO sheets afterreduction.

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CHAPTER – 4

Synthesis of Covalently Connected Graphene Oxide-g-Chiral Polyaniline Nanocomposite With Improved Energy Storage and Chiral Recognition

Introduction:

A unique feature of PANI is doping/dedoping may be carried out reversibly by using simple acid/base chemistry. In the doped state, counter anions stay proximate to the protonated PANI chains (imide group protonation) for electro neutrality. Interactions with these counteranions play a very important role in the morphology of the PANI chains. Chiral counter anions reportedly may induce helicity to the PANI chains depending upon the chirality of the counter anion as in case of doping with D or L-camphor sulfonic acid (CSA).[1] The chiral PANI chains have drawn significant attention for their various applications as in catalysis, chiral recognition, chemical separation or in chemical sensors.[2,3] In this respect GO/chiral PANI nano composite may be very much useful in view of greater surface area provided by the graphene oxide nano sheets. Synthesis of pure PANI chains with the chiral induction by the above strategy or preparation of chiral composite with flexible polyacrylic acid is reported in the literature.[1,4]However, exploration of degree of chiral induction on the PANI chains in presence of rigid and mechanically strong graphene oxide nano sheets during GO/chiral PANI nano composite fabrication is not yet reported and indeed should be very interesting.

Results and Discussion:

In most of the reports of synthesis of PANI in presence of optically pure (D or L)-CSA, the degree of chirality induced is low. Li and Wang for the first time in a very interesting work reported induction of significantly high degree of chirality in PANI chains by optically pure CSA through oxidative polymerization of aniline.[1] In the present work our objective is to prepare covalently attached chiral PANI chains with GO nano sheet surface. Oligomeric aniline moieties attached on GO nano sheets are used for initiation of PANI chains. The polymerization reactions are conducted carefully under inertatmosphere.

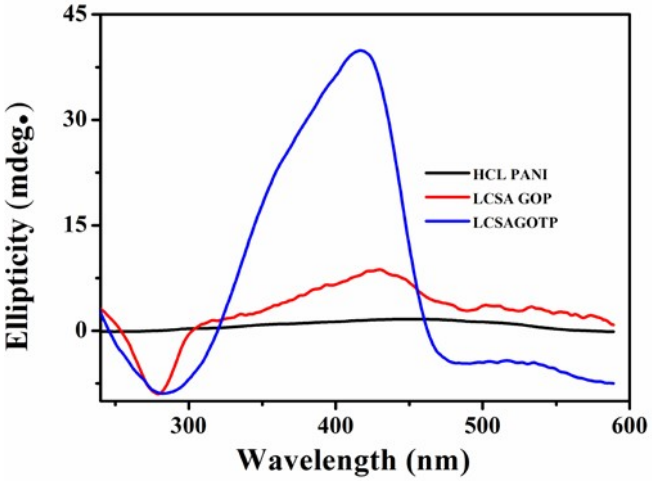
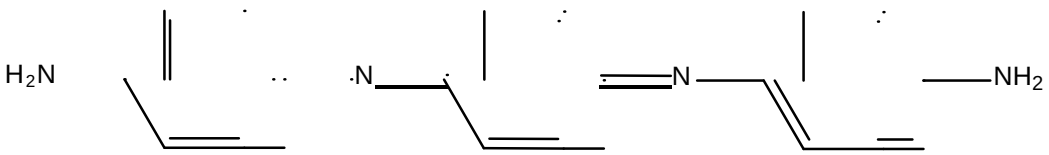


Fig 4.1 CD Spectra of GOTP, GOPL and GOTPL

Figure 4.1 presents the overlay of CD spectra of different GO/PANI nano composites which clearly show that no chirality is induced when the polymerization is conducted in presence of aqueous HCl (GOTP). However, laevorotatory chiral chain formation is noted by relatively weak signal at 430 nm when the polymerization is conducted in presence of GO nano sheets only (samples GOPL and GOTPL). The polymerization condition used here indicates formation of non covalently attached PANI chains. The degree of chiral induction is found to be remarkably increased when trimeric aniline (APQD)(Scheme 4.1) attached GO nano sheets are used.



Scheme 4.1 Structure of APQD

This is attributed to the preferential initiation of chain growth from asymmetric (APQD.L-CSA) adduct at a much faster rate due to significantly lower oxidation

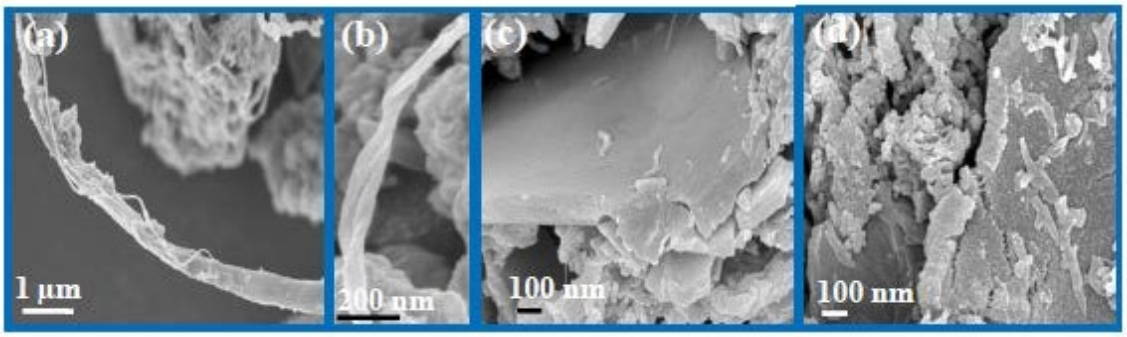


Fig. 4.2 FESEM images of (a & b) GOTPL, (c) GOPL, (d) GOTP

potential of APQD than monomeric aniline. However, under room temperature and high acid conditions, the rate of polymerization being fairly high, numerous PANI chains are also generated due to self nucleation of aniline. Such randomly grown PANI chains are expected to have relatively poor chirality than those initiated from trimeric moieties. This

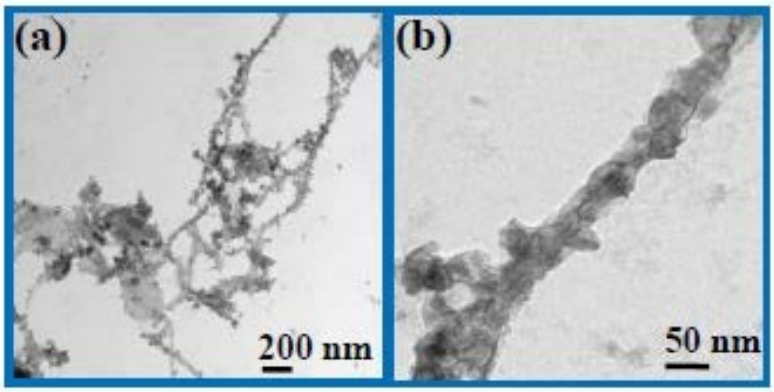


Fig. 4.3 TEM images of (a & b) GOTPL

probably accounts for the broad CD signal observed. The analysis of morphology through FESEM shows formation of clearly visible right handed helical PANI chains (**Figure 4.2**). However, in case of GOPL, helicity of the PANI chains are not observed and importantly non grafted GO nano sheets are clearly visible. In case of GOTP, GO nano sheet anchored PANI cylinders are clearly observed. The HRTEM image of GOTPL also shows formation of helical long PANI chains. (**Figure4.3**).

Overlay of CV curves in **Figure 4.4** shows rectangular nature indicating good charge flow within the electrodes and operation of *EDLC* mechanism. Similarly, the pair of peaks at 0.2(V) and 0.4(V) indicates redox transitions between various PANI oxidation states (leucomeraldine to emaraldine and emaraldine to pernigraniline respectively). The galvanostatic charge discharge experiment (not shown here) results a specific capacitance of

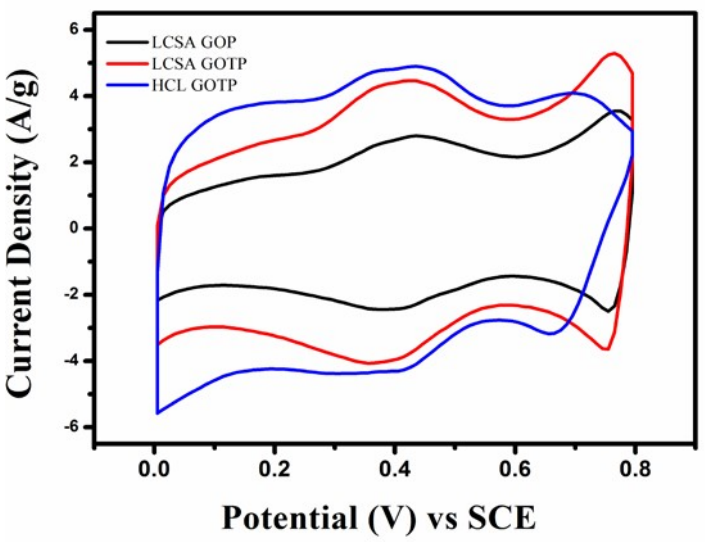


Fig 4.4 CV curves recorded in 1 (M) H_2SO_4 at a scan rate of 10 mV s^{-1}

350 F/g for GOTPL and 240 F/g for GOPL samples which is apparent from the higher enclosed area under the CV curve of GOTPL sample. Therefore, an improved energy storage is found for the GO/chiral PANI nano composite sample where the PANI chains are covalently attached and having higher degree chirality. This is attributed to the covalently connected PANI chains with the GO nano sheet surface helping better synergy between them and helical PANI chains are probably generating higher surface area.

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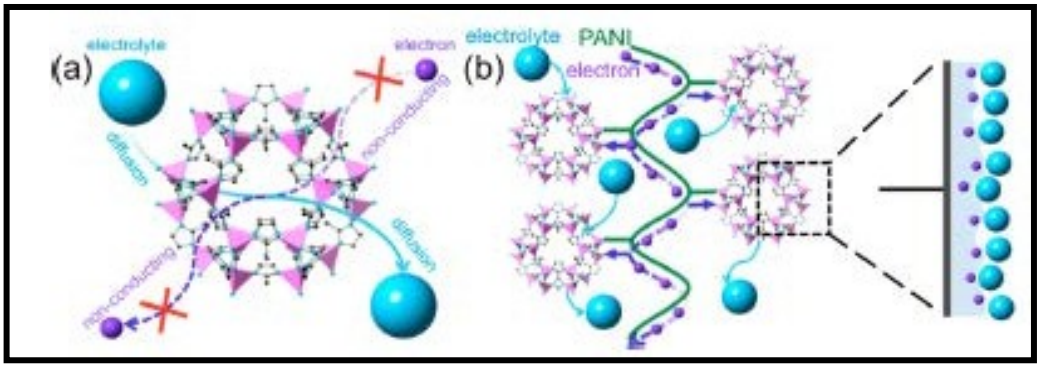
Chapter 5

Summary and Further Extensions

The present thesis work successfully demonstrates a unique method for oligomeric aniline initiated controlled oxidative polymerization of aniline. The efficiency of the developed synthetic method is apparent from the nano structured carbon/PANI hybrid material formation originated from carbon nano material templates nearly excluding any non grafted, randomly connected, uncontrolled PANI chain.[1] The universal nature of the applied synthetic strategy irrespective of the dimensionality (0D, 1D, 2D) of the nano structure templates triggers further research opportunities for the development of tailor made PANI based nano composite materials with component specificmanipulations.

GNS are very much desirable in respect of high conductivity and mechanical strength apart from their high tendency of π-stacking. This may be avoided or at least minimized in GNS/GQD composite where the GQD particles stacked on GNS will inhibit aggregation of GNS.[2] This should make larger available surface area with porosity. All these features are helpful for energy storage following *EDLC* mechanism. In this situation growth of PANI chains will be attempted from GQD particle surfaces following the developed polymerization protocol. Growing relatively shorter PANI chains may be very much effective as it would not block the generated pores appreciably. [3] Furthermore, the *pseudocapacitance* of the PANI chains should operate. In this strategy, mostly the PANI chains should remain sandwiched between the GNS, hence mechanical stress withstanding ability is expected to be higher. The π-stacking interactions between the aromatic rings of PANI chains and those present on the GNS surface should also improve the mechanical properties of the PANI chains. Therefore, significantly improved energy storage may be explained from this planned nano composite which is set for extracting much better synergy between PANI andGNS.

Three dimensional network structure of metal derivatives like oxides, sulphides etc. or metal organic framework (MOF) are having highly porous structure. This increased specific surface area of such porous network structure and possibilities of easier ion movement are advantageous for supercapacitor electrodes operating through *EDLC* mechanism.[4] However, poor conductivity of such network structure seriously limits their said applications. Wang et.al.[5] have reported MOF/PANI nano composite formation for introduction of improved



Scheme-1: Wrapping of MOF with conducting PANI chains[5]

conductivity. In this nano composite, large and randomly connected PANI chains wrap the framework structure and thus provide improved conductivity (Scheme 1). A modified strategy may be put forward where GQD nano particles will be entered inside the pores of the MOF and then controlled growth of PANI chains will be affected from them. This would generate a MOF based nano composite material with much improved conductivity. Hence a significant improvement in energy storage isexpected.

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List of Publications:

1)"*Candle soot derived Carbon nanodot/Polyaniline Hybrid Materials through Controlled Grafting of Polyaniline Chains for Supercapacitors"* **Tapas Ghosh,** Radhakanta Ghosh, Udayan Basak, Soumabrata Majumder, Ranadeb Ball, Debasish Mandal, Arun K. Nandi and Dhruba. P. Chatterjee ***J. Mater. Chem. A,* 2018*, 6,* 6476-6492.**

2) Synthesis of 'living' poly(2-dimethylaminoethyl methacrylate) and stimuli responsive/multifunctional block copolymers effective in fabrication of CdS'smart' 'Q-Particles' Udayan Basak, Radhakanta Ghosh, **Tapas Ghosh**, Soumabrata Majumdar, Mahuya Pakhira,Tuhin Ghosh, Dhruba P. Chatterjee ***Polymer*, 2018, 155,27–41.**

Papers presented in International/National Conference :

1) 'Controlled Growth of Polyaniline Chains from the Surface of Graphene Nano Sheets using 'Grafting from' Approach' (Abstract Code -T02_02), **Poster** presented in **National Conference on Recent Developments in Nanoscience and Nanotechnology**; January 29-31, 2019 at Jadavpur University, Kolkata.
2) 'Synthesis of Chiral Graphene-Polyaniline Hybrid Material' (Abstract ID – 205), **Oral** presentation in International Conference on '**Current Trends in Materials Science and Engineering'**; January 19-20, 2018 at S.N. Bose National Centre for Basic Sciences, Kolkata.
3) 'An approach for controlled grafting of PANI chains from fluorescent carbon nanodots' (Abstract Code-MACRO 232), **Poster** presented in **International Conference on Polymer Science and Technology**; January 8-11, 2017 at Thiruvananthapuram,India.
4) 'An Approach for Controlled Grafting of PANI Chains from Fluorescent Carbon Nano Particles' (Abstract Code-P20), **Poster** presented in **International IUPAC Conference on Polymer-Solvent Complexes and Intercalates**; January 27-30, 2016 at Indian Association of Cultivation of Science,Kolkata.

Forwarded

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